A New Route to Enol Ethers

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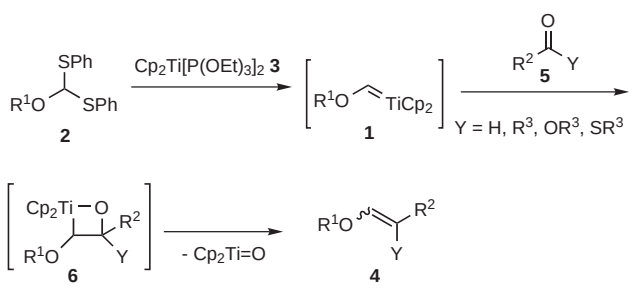
Dedicated to Professor Teruaki Mukaiyama on the occasion of his 77th birthday

Abstract: Dithioorthoformates having various alkoxy groups were obtained by copper(II) bromide-promoted oxidative coupling of bis(phenylthio)methyltributylstannane with alcohols. The dithioorthoformates thus prepared are useful precursors for alkoxymethylidene complexes of titanium, which transform carbonyl compounds into a variety of enol ethers. Even the alkoxymethylidene complexes having a terminal olefin moiety can be prepared and employed for carbonyl olefination without formation of ring-closing metathesis product.

Key words: carbene complexes, esters, ketones, olefination, titanium

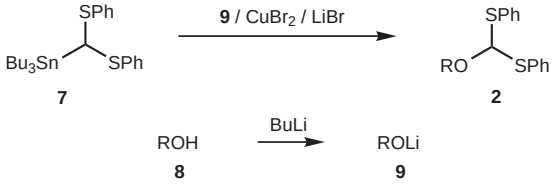
Considerable effort has been made to develop efficient methods for preparation of enol ethers because of their usefulness as synthetic intermediates. While carbonyl olefinations utilizing α-phosphorous[1] and α-silyl[2] carbanions bearing a α-alkoxy group are considered as major approaches to the enol ethers, these reactions cannot be employed for the transformation of carboxylic acid derivatives such as esters and lactones. We have eliminated this difficulty by means of the alkoxymethylidene complex of titanium **1** generated by the desulfurization of methoxybis(phenylthio)methane **2** (R^1 = Me) with titanocene(II) reagent $Cp_2Ti[P(OEt)_3]_2$ **3** (Scheme 1).[3] This procedure provides a convenient way for the preparation of 1,2-diheteroatom-substituted olefins **4** from carboxylic acid derivatives **5** via the oxatitanacyclobutane intermediates **6**. A serious drawback remained in this procedure; it is difficult to introduce a variety of alkoxy groups to the olefinating agents due to lack of easy access to dithioorthoformates **2**.



Scheme 1

In this context, we recently developed an alkoxylmethyl chloride–titanocene(II) system as an alternative method for alkoxymethylidenation of carbonyl compounds.[4] Although this new method enables us to prepare various 1-alkoxy-1-alkenes, preparation of starting alkoxymethyl chlorides from acid labile alcohols is difficult and the reaction requires essentially more than two equivalents of alkoxymethyl chloride.

Then we turned our attention to the preparation of dithioorthoformates **2** from various alcohols under mild reaction conditions and their application to carbonyl olefination. Preparation of dithioorthoformates is generally performed by the reaction of alkyl dichloroalkyl ethers[5] with alkali metal thiolates. However this procedure cannot be applied for synthesis of dithioorthoformates bearing an acid labile alkoxy group. Although several other methods for the preparation of dithioorthoformates have been developed, they all need use of a large excess amount of alcohol and multi-step procedures, hence they are of limited synthetic utility.[6] Previously we found that the oxidative coupling of allyl and vinylstannanes with nucleophiles such as alcohols, acetates, amines, enol silyl ethers, and allylsilanes proceeded in the presence of copper(II) salts.[7] These results prompted us to investigate the copper(II) salt-promoted oxidative coupling of readily available bis(phenylthio)methyltributylstannane **7** and alcohols **8** (Scheme 2). Here we describe a versatile method for the preparation of dithioorthoformates **2** from alcohols and their application to alkoxymethylidenation of carbonyl compounds leading to the formation of a variety of enol ethers.



Scheme 2

Initially the transformation of benzyl alcohol **8a** to the corresponding dithioorthoformate **2a** with bis(phenylthio)methylstannane **7** was investigated under various conditions. When lithium benzyloxide **9a** prepared in situ from **8a** and *n*-butyllithium was treated with bis(phenylthio)methylstannane **7** at –40 ºC in the presence of $CuBr_2$, the dithioorthoformate **2a** was produced in 30% yield

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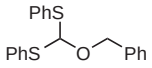
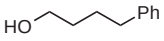
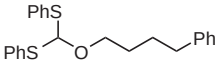
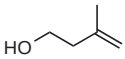
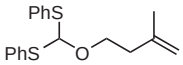
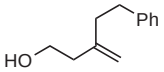
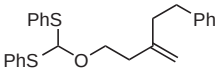
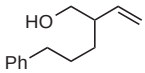
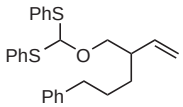
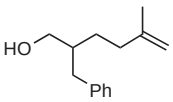
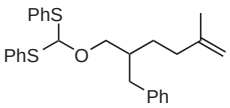
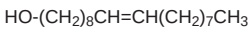
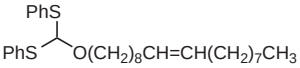
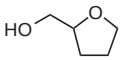
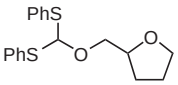
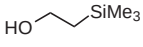
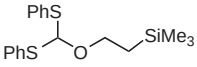
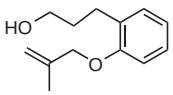
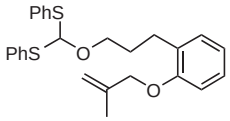
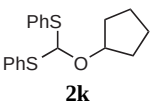
along with a considerable amount of tris(phenylthio)methane. An improved yield (71%) of the product **2a** was obtained when LiBr was used as an additive. In this reaction, neither inorganic base such as K_2CO_3 nor Et_3N was suitable as a base giving poor yield of **2a**. Under optimized conditions, the reactions of a variety of alcohols **8** with **7** were preformed and the corresponding dithioorthoformates **2** were obtained in good yields (Table 1). It is noteworthy, from a synthetic point of view, that this transformation is applicable to the unsaturated alcohols and acid labile alcohols such as 2-(trimethylsilyl)ethanol. The secondary alcohols such as cyclopentanol **8k** also reacted with **7** to give the corresponding dithioorthoformates **2k** though the yields were unsatisfactory (entry 11).

Barton et al. suggested that copper(II) salt promoted oxidative coupling reactions of triarylbismuths and triarylbismuth diacetates with heteroatom nucleophiles proceed via formation of a certain trivalent arylcopper species.[8]

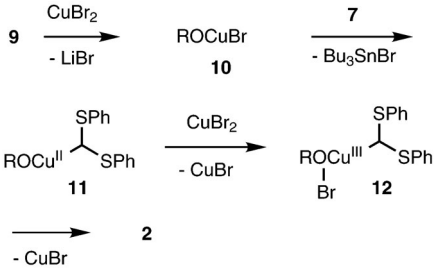
Table 1 Preparation of Dithioorthoformates **2** from Alcohols **8** by Copper(II) Bromide-Promoted Reaction with Bis(phenylthio)methylstannane **7**[a]

Entry	Alcohol **8**	Dithioorthoformate **2**	Yield (%)
1	 **8a**	 **2a**	71
2	 **8b**	 **2b**	58
3	 **8c**	 **2c**	65
4	 **8d**	 **2d**	73
5	 **8e**	 **2e**	73
6	 **8f**	 **2f**	51
7	 **8g**	 **2g**	67
8	 **8h**	 **2h**	74
9	 **8i**	 **2i**	78
10	 **8j**	 **2j**	76
11	 **8k**	 **2k**	49

[a] All the reactions were performed with a procedure similar to that described in the text.

Recently copper(II) salt-promoted cross-couplings of arylboronic acids[9] with heteroatom nucleophiles were investigated, and these reactions are believed to follow a similar reaction pathway. We also assume that the formation of dithioorthoformates **2** is explained by the reaction path involving the formation of organocopper(III) intermediate depicted in Scheme 3. First the alkoxycopper(II) bromide **10** is produced by the reaction of lithium alkoxide **9** with copper(II) bromide. The transmetallation between bis(phenylthio)methyltributylstannane **7** and **10** affords the bis(phenylthio)methylcopper(II) species **11**. The dithioorthoformate **2** is formed by one-electron oxidation of **11** and subsequent reductive elimination of the trivalent organocopper species **12**.

Despite the above arguments, however, an alternative pathway for the present reaction, in which a cation radical intermediate is formed by the oxidation of **7** with copper(II) salt should not be excluded. Mizuno et al. described an oxidative coupling of benzylsatnnanes with alcohols in which a cation radical species is formed by the oxidation of benzylstannanes with copper(II) salt under irradiation.[10] Narasaka and his co-workers reported similar oxidative couplings of 2-tributylstannyl-1,3-dithianes with olefinic nucleophiles using ammonium hexanitratocerate(IV) or ferrocenium hexafluorophosphate and they suggested that the active intermediate of this reaction is 1,3-dithian-2-yl cation.[11] The related formation of acetals by electrochemical oxidation of alkoxymethylstannanes in the presence of alcohols was also reported.[12] As for acceleration of the reaction with lithium bromide, we tentatively assume that it is attributable to increase in solubility of $CuBr_2$ through the formation of a certain cuprate[13] or generation of a highly coordinated organotin species from the stannylthioacetal **7** which facilitates its oxidation with $CuBr_2$.[14]



Scheme 3

Next the carbonyl olefination utilizing these dithioorthoformates **2** was investigated. The dithioorthoformates **2** were treated with the titanocene(II) reagent **3** (4.5 equiv) for 10 minutes and then with ketones **5a**–**d** to afford the corresponding enol ethers in good yields (Table 2). As is the case with other carbonyl olefination procedures using the Schrock-type transition metal carbene complexes,[15] the present alkoxymethylidenation could be applied to carboxylic acid derivatives such as esters, lactones, thiolesters, and amides to afford the diheteroatom-substituted alkenes in good yields (Table 3). The *E*-isomers were almost always predominant in these reactions. The observed selectivity agrees well with that of the alkoxymethylidenation of the carboxylic acid derivatives using organotitanium species generated from alkoxymethyl chlorides and the titanocene(II) reagent[4] suggesting that the reaction proceeds via an oxatitanacyclobutane intermediate **6** in which dipole-dipole repulsion between an alkoxy substituent (R^1O) and a polar substituent (Y) is minimized.

What is striking is the fact that no ring-closing metathesis proceeded when the dithioorthoformates bearing a terminal olefin moiety were employed and the resulting titanocene alkoxymethylidenes react with carbonyl compounds to form enol ethers.[16] We found that a variety of unsaturated carbo and heterocyclic compounds were obtained by the treatment of thioacetals possessing a terminal double bond with the titanocene(II) species.[17] Therefore the difference of reactivity towards carbon-carbon double bond between alkylidene and alkoxymethylidene complexes is of great interest because this finding indicates that the reactivity of titanium carbene complexes is largely affected by the electronic property of α-heteroatom substituent.

In conclusion, we have established a versatile method for the preparation of dithioorthoformates from various alcohols including ones possessing an acid labile group. These dithioorthoformates are useful for the preparation of a variety of heteroatom-substituted olefins. Further study on the elucidation of reactivity of heteroatom-substituted titanium carbene complexes and their application to organic synthesis is now in progress.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using TMS as internal standard. Chemical shifts (δ) are quoted in ppm from TMS for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. IR absorptions are reported in cm^{-1}. All reactions were performed under argon atmosphere in dried glassware. THF was distilled from Na and benzophenone. Preparative thin layer chromatography (PTLC) was carried out using Wakogel B-5F.

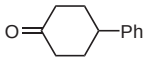
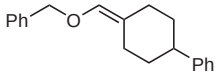
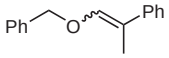
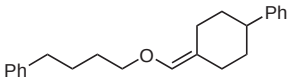
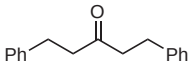
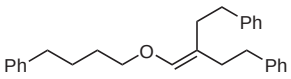
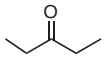
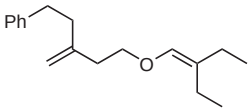
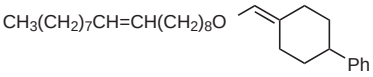
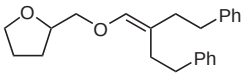
Reaction of Benzyl Alcohol (8a) with Bis(phenylthio)methyltributylstannane (7); General Procedure

Lithium bromide (174 mg, 2.00 mmol) was placed in a flask and dried by heating with a heat gun under reduced pressure (2-3 mmHg). After cooling, a THF (4 mL) solution of **8a** (108 mg, 1.00 mmol) was added under argon. A hexane (1.47 M, 0.68 mL) solution of *n*-BuLi (1.0 mmol) was added at 0 °C, and the mixture was stirred for 15 min. Copper(II) bromide (491 mg, 2.20 mmol) and a THF (4 mL) solution of **7** (521 mg, 1.00 mmol) were successively added with an interval of 15 min to the reaction mixture which was cooled to –40 °C. After stirring for 2 h at –40 °C, the reaction was quenched by addition of 3.5% aq NH_3 solution. The organic materials were extracted with Et_2O and dried over K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by silica gel PTLC (hexane) to yield benzyloxybis(phenylthio)methane (**2a**) (241 mg, 71%). In a similar manner, the dithioorthoformates **2b**–**k** were also obtained.

Benzyloxybis(phenylthio)methane (2a)

IR (neat): 3063, 3030, 2955, 2854, 1594, 1455, 1376, 1079, 1045, 1024, 741, 696, 672 cm^{-1}.

Table 2 Titanocene(II)-Promoted Alkoxymethylidenation of Ketones **5** Using Dithioorthoformates **2**[a]

Entry	Dithioorthoformate **2**	Carbonyl compound **5**	Product **4**	Yield (%) (*E*:*Z*)[b]
1	**2a**	 **5a**	 **4a**	56
2	**2a**	 **5b**	 **4b**	55 (74:26)
3	**2b**	**5a**	 **4c**	58
4	**2b**	 **5c**	 **4d**	70
5	**2d**	 **5d**	 **4e**	63
6	**2g**	**5a**	 **4f**	56
7	**2f**	**5c**	 **4g**	54

[a] All the reactions were performed with a procedure similar to that described in the text.
[b] Determined by NMR analysis.

^{1}H NMR ($CDCl_3$): δ = 4.85 (s, 2 H), 6.26 (s, 1 H), 7.08–7.11 (m, 2 H), 7.23–7.33 (m, 9 H), 7.49–7.53 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 67.8, 92.5, 127.9, 128.0, 128.26, 128.34, 129.0, 132.6, 133.4, 136.4.

Anal. Calcd for $C_{20}H_{18}OS_2$: C, 70.97; H, 5.36. Found: C, 70.80; H, 5.47.

1-Bis(phenylthio)methoxy-4-phenylbutane (2b)
IR (neat): 3060, 3025, 2938, 2862, 1582, 1479, 1439, 1385, 1065, 1025, 740, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.55–1.58 (m, 4 H), 2.54 (t, *J* = 7.1 Hz, 2 H), 3.79 (t, *J* = 5.8 Hz, 2 H), 6.18 (s, 1 H), 7.09–7.14 (m, 2 H), 7.17–7.32 (m, 9 H), 7.46–7.50 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 27.8, 28.6, 35.4, 65.9, 93.3, 125.7, 127.9, 128.2, 128.4, 128.9, 132.4, 133.8, 142.2.

Anal. Calcd for $C_{23}H_{24}OS_2$: C, 72.59; H, 6.36. Found: C, 72.75; H, 6.42.

4-Bis(phenylthio)methoxy-2-methylbut-1-ene (2c)
IR (neat): 3074, 2937, 2879, 1650, 1582, 1478, 1439, 1375, 1303, 1157, 1056, 1024, 891, 615 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 3 H), 2.23 (t, *J* = 6.8 Hz, 2 H), 3.90 (t, *J* = 6.8 Hz, 2 H), 4.66 (s, 1 H), 4.73 (s, 1 H), 6.22 (s, 1 H), 7.25–7.34 (m, 6 H), 7.49–7.52 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 22.5, 37.1, 64.2, 93.4, 111.8, 127.9, 128.9, 132.4, 133.8, 142.2.

Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.65; H, 6.41.

4-Bis(phenylthio)methoxy-2-phenethylbut-1-ene (2d)
IR (neat): 3060, 3025, 2937, 1646, 1582, 1479, 1439, 1156, 1052, 1025, 895, 741 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.25 (t, *J* = 7.7 Hz, 2 H), 2.28 (t, *J* = 6.2 Hz, 2 H), 2.68 (dd, *J* = 7.1, 9.3 Hz, 2 H), 3.91 (t, *J* = 6.9 Hz, 2 H), 4.74 (s, 1 H), 4.78 (s, 1 H), 6.23 (s, 1 H), 7.12–7.35 (m, 11 H), 7.47–7.52 (m, 4 H).

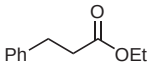
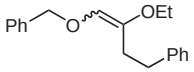
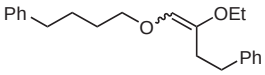
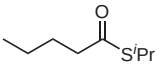
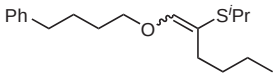
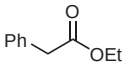
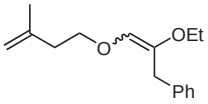
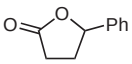
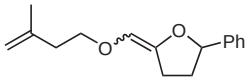
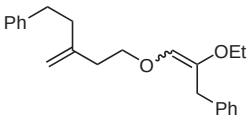
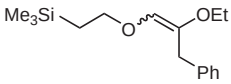
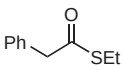
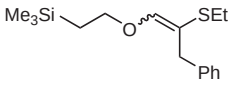
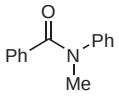
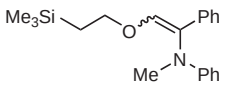
^{13}C NMR ($CDCl_3$): δ = 34.1, 35.6, 37.9, 64.3, 93.4, 111.2, 125.8, 127.9, 128.27, 128.29, 128.9, 132.3, 133.8, 141.9, 145.5.

Anal. Calcd for $C_{25}H_{26}OS_2$: C, 73.85; H, 6.45. Found: C, 73.66; H, 6.54.

3-[Bis(phenylthio)methoxy]methyl-6-phenylhex-1-ene (2e)
IR (neat): 3060, 3025, 2932, 2858, 1582, 1496, 1479, 1453, 1382, 1303, 1059, 1025, 916, 741, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.18–1.27 (m, 1 H), 1.34–1.61 (m, 3 H), 2.19–2.27 (m, 1 H), 2.45–2.53 (m, 2 H), 3.70 (d, *J* = 6.1 Hz, 2 H), 4.958 (d, *J* = 15.8 Hz, 1 H), 4.964 (d, *J* = 11.6 Hz, 1 H), 5.44–5.56 (m, 1 H), 6.22 (s, 1 H), 7.10–7.33 (m, 11 H), 7.47–7.53 (m, 4 H).

Table 3 Titanocene(II)-Promoted Alkoxymethylidenation of Carboxylic Acid Derivatives **5** Using Dithioorthoformates **2**[a]

Entry	Dithioorthoformate **2**	Carbonyl compound **5**	Product **4**	Yield (%) (*E*:*Z*)[b]
1	**2a**	 **5e**	 **4h**	57 (47:53)[c]
2	**2b**	**5e**	 **4i**	74 (56:44)[c]
3	**2b**	 **5f**	 **4j**	85 (82:18)
4	**2c**	 **5g**	 **4k**	51 (61:39)
5	**2c**	 **5h**	 **4l**	52 (62:38)[d]
6	**2d**	**5g**	 **4m**	80 (62:38)
7	**2i**	**5g**	 **4n**	62 (58:42)
8	**2i**	 **5h**	 **4o**	81 (83:17)
9	**2i**	 **5i**	 **4p**	64[e]

[a] All the reactions were performed with a procedure similar to that described in the text.
[b] Based on the isolated yields.
[c] Determined by NMR analysis.
[d] Ratio of the stereoisomers.
[e] Obtained as a single stereoisomer. The configuration was not determined.

^{13}C NMR ($CDCl_3$): δ = 28.8, 30.8, 35.9, 43.4, 69.0, 93.3, 115.9, 125.6, 127.80, 127.83, 128.2, 128.3, 128.9, 132.3, 132.4, 132.7, 133.71, 133.74, 139.5, 142.5.

Anal. Calcd for $C_{26}H_{28}OS_2$: C, 74.24; H, 6.71. Found: C, 74.21; H, 6.57.

5-Benzyl-6-bis(phenylthio)methoxy-2-methylhex-1-ene (2f)
IR (neat): 3060, 3025, 2930, 1648, 1582, 1495, 1479, 1452, 1439, 1374, 1056, 1025, 887, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.33–1.44 (m, 2 H), 1.59 (s, 3 H), 1.74–1.80 (m, 1 H), 1.92–1.98 (m, 2 H), 2.48 (dd, *J* = 6.3, 13.2 Hz, 1 H), 2.55 (dd, *J* = 7.2, 13.2 Hz, 1 H), 3.63 (dd, *J* = 9.4, 18.2 Hz, 1 H), 3.65 (dd, *J* = 9.2, 18.3 Hz, 1 H), 4.58 (s, 1 H), 4.65 (s, 1 H), 6.17 (s, 1 H), 6.99–7.01 (m, 2 H), 7.15–7.33 (m, 9 H), 7.46–7.51 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 22.3, 28.6, 34.9, 37.7, 39.6, 67.9, 93.6, 110.0, 125.8, 127.8, 127.9, 128.1, 128.3, 128.91, 128.93, 129.2, 132.4, 132.6, 133.7, 135.3, 140.5, 145.6.

Anal. Calcd for $C_{27}H_{30}OS_2$: C, 74.61; H, 6.96. Found: C, 74.38; H, 7.00.

1-[Bis(phenylthio)methoxy]octadec-9-ene (2g)
IR (neat): 3060, 3004, 2925, 2853, 1583, 1479, 1466, 1439, 1378, 1303, 1156, 1065, 1025, 967, 737, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H), 1.17–1.40 (m, 22 H), 1.45–1.58 (m, 2 H), 1.90–2.00 (m, 4 H), 3.76 (t, *J* = 6.4 Hz, 2

H), 5.30–5.41 (m, 2 H), 6.18 (s, 1 H), 7.26–7.33 (m, 4 H), 7.49–7.52 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 26.1, 27.2, 29.1, 29.2, 29.27, 29.31, 29.4, 29.5, 29.8, 31.9, 66.2, 93.3, 127.8, 128.9, 129.8, 123.0, 132.4, 133.9.

Anal. Calcd for $C_{31}H_{46}OS_2$: C, 74.64; H, 9.29. Found: C, 74.45; H, 9.08.

2-[Bis(phenylthio)methoxy]methyloxolane (2h)
IR (neat): 3058, 2946, 1582, 1479, 1439, 1304, 1057, 1025, 1000, 919, 740, 710, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.47–1.57 (m, 1 H), 1.76–1.92 (m, 3 H), 3.67–3.85 (m, 4 H), 3.98 (tt, *J* = 6.0, 6.0 Hz, 1 H), 6.29 (s, 1 H), 7.25–7.34 (m, 6 H), 7.50–7.55 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 25.5, 28.1, 67.7, 68.2, 77.0, 93.3, 127.8, 127.9, 128.9, 132.2, 132.5, 133.7.

Anal. Calcd for $C_{18}H_{20}OS_2$: C, 65.02; H, 6.06. Found: C, 64.92; H, 5.94.

1-Bis(phenylthio)methoxy-2-(trimethylsilyl)ethane (2i)
IR (neat): 3060, 2952, 2896, 1582, 1479, 1439, 1376, 1249, 1177, 1059, 1087, 1025, 938, 836, 739, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.83–0.89 (m, 2 H), 3.84–3.90 (m, 2 H), 6.18 (s, 1 H), 7.27–7.36 (m, 6 H), 7.51–7.54 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = –1.5, 17.6, 64.0, 93.1, 127.8, 128.9, 132.4, 133.9.

Anal. Calcd for $C_{18}H_{24}OSiS_2$: C, 62.02; H, 6.94. Found: C, 62.23; H, 6.80.

1-[3-[Bis(phenylthio)methoxy]propyl]-2-(2-methylprop-2-enyloxy)benzene (2j)
IR (neat): 3074, 3060, 2938, 2870, 1657, 1600, 1584, 1492, 1479, 1451, 1438, 1376, 1301, 1239, 1192, 1120, 1054, 1024, 903, 751 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.81 (s, 3 H), 1.81–1.90 (m, 2 H), 2.61 (t, *J* = 7.7 Hz, 2 H), 3.80 (t, *J* = 6.4 Hz, 2 H), 4.40 (s, 2 H), 4.95 (s, 1 H), 5.08 (s, 1 H), 6.17 (s, 1 H), 6.78–6.85 (m, 2 H), 6.97 (dd, *J* = 1.7, 7.3 Hz, 1 H), 7.13 (dt, *J* = 1.8, 7.8 Hz, 1 H), 7.24–7.34 (m, 6 H), 7.47–7.54 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 19.5, 27.2, 29.1, 66.1, 71.4, 93.4, 111.3, 112.1, 120.4, 127.0, 127.9, 128.9, 130.0, 130.2, 132.5, 133.8, 141.0, 156.5.

Anal. Calcd for $C_{26}H_{28}O_2S_2$: C, 71.52; H, 6.46. Found: C, 71.40; H, 6.56.

[Bis(phenylthio)methoxy]cyclopentane (2k)
IR (neat): 3059, 2960, 2745, 1582, 1477, 1439, 1362, 1319, 1302, 1172, 1051, 1025, 968, 743, 710, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.37–1.65 (m, 8 H), 4.41–4.45 (m, 1 H), 5.91 (d, *J* = 1.3 Hz, 1 H), 7.21–7.33 (m, 6 H), 7.47–7.56 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 23.3, 32.2, 79.9, 92.2, 128.0, 128.7, 133.3.

Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.72; H, 6.63.

Olefination of 4-Phenylcyclohexanone (5a) with 2a; General Procedure
Finely powdered molecular sieves 4A (135 mg), magnesium turnings (39 mg, 1.6 mmol) and Cp_2TiCl_2 (336 mg, 1.35 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure. After cooling, THF (3 mL) and $P(OEt)_3$ (0.46 mL, 2.7 mmol) were added successively with stirring at 25 °C under argon, and the reaction mixture was stirred for 3 h. A THF (1 mL) solution of **2a** (152 mg, 0.45 mmol) was added to the mixture and stirring was continued for 10 min at the same temperature. A THF (1 mL) solution of **5a** (52 mg, 0.30 mmol) was added dropwise over 10 min and the reaction mixture was refluxed for 3 h. After cooling to r.t., the reaction was quenched by addition of 1 M NaOH. Insoluble materials were filtered off through Celite and washed with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried over K_2CO_3 and the solvent was removed under reduced pressure. The residue was purified by PTLC (hexane–EtOAc, 95:5) to afford 1-benzyloxymethylidene-4-phenylcyclohexane (**4a**) (47 mg, 56%). In a similar manner, the enol ethers **4b**–**p** were also obtained.

1-Benzyloxymethylidene-4-phenylcyclohexane (4a)
IR (neat): 3083, 3028, 2923, 2854, 1686, 1602, 1494, 1453, 1444, 1360, 1205, 1181, 1133, 1077, 1064, 1027, 752, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.28–1.50 (m, 2 H), 1.75–2.18 (m, 5 H), 2.62 (tt, *J* = 3.3, 12.2 Hz, 1 H), 3.00 (d, *J* = 13.6 Hz, 1 H), 4.76 (s, 2 H), 5.95 (t, *J* = 1.7 Hz, 1 H), 7.17–7.39 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 25.5, 30.4, 34.3, 35.6, 44.7, 73.5, 118.2, 125.9, 126.8, 127.4, 127.7, 128.3, 128.4, 137.5, 137.9, 147.2.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.40; H, 8.04.

Benzyl 2-Phenylprop-1-enyl Ether (4b)
IR (neat): 3056, 3031, 2928, 2865, 1651, 1599, 1496, 1454, 1444, 1374, 1282, 1264, 1206, 1161, 1072, 1028, 909, 845, 758, 736, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.90–1.91 (m, 0.78 H), 2.04–2.05 (m, 2.22 H), 4.89 (s, 0.52 H), 4.92 (s, 1.48 H), 6.25 (br q, *J* = 1.3 Hz, 0.26 H), 6.56 (br q, *J* = 1.3 Hz, 0.74 H,), 7.14–7.68 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 12.8, 18.4, 74.0, 74.3, 111.3, 115.2, 125.0, 125.9, 126.0, 127.2, 127.3, 127.5, 127.84, 127.88, 127.91, 128.3, 128.50, 128.52, 137.5, 137.6, 140.6, 142.9, 143.5.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.72; H, 7.16.

4-Phenyl-1-[(4-phenylbutoxy)methylidene]cyclohexane (4c)
IR (neat): 3026, 2923, 2858, 1686, 1603, 1494, 1452, 1443, 1204, 1188, 1142, 1082, 1064, 840, 749, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.37–1.51 (m, 2 H), 1.63–1.83 (m, 5 H), 1.91–2.18 (m, 4 H), 2.55–2.67 (m, 3 H), 2.93 (d, *J* = 11.9 Hz, 1 H), 3.69 (t, *J* = 7.0 Hz, 2 H), 5.83 (s, 1 H), 7.14–7.20 (m, 6 H), 7.25–7.30 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 25.4, 27.7, 29.3, 30.5, 34.4, 35.6, 35.7, 44.8, 71.6, 117.1, 125.7, 125.9, 126.8, 128.3, 128.4, 137.9, 142.3, 147.2.

Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 85.85; H, 9.07.

2-Phenethyl-4-phenylbut-1-enyl 4-Phenylbutyl Ether (4d)
IR (neat): 3084, 3062, 3026, 2935, 2858, 1674, 1602, 1496, 1453, 1179, 1133, 1076, 1030, 843, 746, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.52–1.73 (m, 4 H), 2.17 (t, *J* = 7.8 Hz, 2 H), 2.42 (t, *J* = 8.1 Hz, 2 H), 2.60–2.74 (m, 6 H), 3.60 (t, *J* = 6.1 Hz, 2 H), 5.78(s, 1 H), 7.13–7.29 (m, 15 H).

^{13}C NMR ($CDCl_3$): δ = 27.7, 29.2, 29.3, 33.9, 34.2, 35.1, 35.6, 71.6, 116.9, 125.6, 125.69, 125.72, 128.15, 128.22, 128.3, 128.37, 128.40, 141.8, 142.27, 142.31, 142.7.

Anal. Calcd for $C_{28}H_{32}O$: C, 87.45; H, 8.39. Found: C, 87.50; H, 8.26.

2-Ethylbut-1-enyl 3-Phenethylbut-3-enyl Ether (4e)
IR (neat): 3064, 3027, 2963, 1677, 1644, 1496, 1455, 1372, 1269, 1160, 1079, 893, 839, 745, 698 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 6.5 Hz, 3 H), 1.92 (dq, *J* = 7.5, 1.2 Hz, 2 H), 2.08 (q, *J* = 7.6 Hz, 2 H), 2.33–2.39 (m, 4 H), 2.76 (dd, *J* = 7.0, 9.4 Hz, 2 H), 3.77 (t, *J* = 7.1 Hz, 2 H), 4.81 (s, 1 H), 4.84 (s, 1 H), 5.77 (s, 1 H), 7.15–7.20 (m, 3 H), 7.24–7.30 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 12.6, 13.2, 20.1, 24.3, 34.3, 36.3, 38.2, 70.5, 111.1, 122.3, 125.8, 128.29, 128.32, 139.3, 142.0, 145.8.

Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.50; H, 10.33.

1-[Octadec-9-enyloxymethylidene]-4-phenylcyclohexane (4f)
IR (neat): 3026, 3003, 2924, 2853, 1687, 1639, 1602, 1493, 1456, 1369, 1204, 1186, 1142, 839, 754 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25–2.20 (m, 35 H), 2.62 (tt, *J* = 12.2, 3.2 Hz, 1 H), 2.93 (d, *J* = 13.8 Hz, 1 H), 3.68 (t, *J* = 6.7 Hz, 2 H), 5.35 (t, *J* = 4.7 Hz, 2 H), 5.85 (s, 1 H), 7.15–7.33 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 25.4, 25.9, 27.2, 29.2, 29.3, 29.4, 29.47, 29.52, 29.71, 29.74, 29.8, 30.5, 31.9, 34.4, 35.5, 35.7, 44.8, 71.9, 116.9, 125.9, 126.80, 126.85, 128.3, 129.8, 129.9, 131.1, 138.0, 147.3.

Anal. Calcd for $C_{31}H_{50}O$: C, 84.87; H, 11.49. Found: C, 84.69; H, 11.21.

2-[(2-Phenethy-4-phenylbut-1-enyl)oxymethyl]oxolane (4g)
IR (neat): 3025, 2925, 2859, 1674, 1603, 1496, 1454, 1277, 1175, 1156, 1127, 1076, 1030, 746, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.63–1.73 (m, 1 H), 1.82–1.96 (m, 3 H), 2.18 (t, *J* = 8.0 Hz, 2 H), 2.40–2.51 (m, 2 H), 2.60–2.81 (m, 4 H), 3.56–3.66 (m, 2 H), 3.72–3.88 (m, 2 H), 3.97–4.05 (m, 1 H), 5.86 (s, 1 H), 7.14–7.30 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 26.1, 28.2, 29.5, 34.1, 34.4, 35.3, 68.7, 74.3, 77.8, 117.3, 125.9, 126.0, 128.4, 128.5, 128.66, 128.72, 142.4, 142.6, 142.9.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.39; H, 8.39. Found: C, 81.98; H, 8.66.

Benzyl 2-Ethoxy-4-phenylbut-1-enyl Ether (4h)
IR (neat): 3028, 2977, 2927, 2866, 1686, 1604, 1496, 1454, 1382, 1170, 1131, 1077, 1056, 746, 698 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.26 (t, *J* = 7.0 Hz, 1.59 H), 1.27 (t, *J* = 7.0 Hz, 1.41 H), 2.18 (t, *J* = 7.7 Hz, 1.06 H), 2.54 (t, *J* = 7.8 Hz, 0.94 H), 2.71–2.76 (m, 2 H), 3.57 (q, *J* = 7.4 Hz, 0.94 H), 4.00 (q, *J* = 7.0 Hz, 1.06 H), 4.44 (s, 0.94 H), 4.68 (s, 1.06 H), 5.44 (s, 0.53 H), 5.77 (s, 0.47 H), 7.14–7.36 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 14.9, 15.7, 29.9, 32.7, 33.2, 33.9, 63.1, 65.7, 74.0, 74.6, 125.6, 125.71, 125.74, 127.4, 127.71, 127.74, 128.1, 128.2, 128.33, 128.37, 128.44, 128.56, 128.63, 137.6, 137.7, 138.4, 141.8, 142.2, 147.2.

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.66; H, 8.14.

2-Ethoxy-4-phenylbut-1-enyl 4-Phenylbutyl Ether (4i)
IR (neat): 3061, 3026, 2975, 2935, 2862, 1687, 1604, 1496, 1454, 1232, 1175, 1136, 1077, 1056, 747, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.265, 1.273 (t, *J* = 7.1, 6.9 Hz, 3 H), 1.52–1.71 (m, 4 H), 2.19 (dd, *J* = 7.5, 8.2 Hz, 0.88 H), 2.52 (dd, *J* = 6.7, 9.1 Hz, 1.12 H), 2.59–2.65 (m, 2 H), 2.72–2.80 (m, 2 H), 3.42 (t, *J* = 6.2 Hz, 0.88 H), 3.55–3.64 (m, 2 H), 3.98 (q, *J* = 7.0 Hz, 1.12 H), 5.34 (s, 0.44 H), 5.69 (s, 0.56 H), 7.15–7.29 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 14.9, 15.7, 27.6, 27.8, 29.1, 29.2, 29.8, 32.8, 33.3, 34.0, 35.5, 35.6, 63.2, 65.6, 72.3, 72.5, 125.60, 125.69, 125.72, 126.3, 128.1, 128.2, 128.3, 128.37, 128.44, 128.5, 129.3, 137.7, 141.9, 142.1, 142.26, 142.32, 146.5.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.60.

(*E*)-2-(Isopropylthio)hex-1-enyl 4-Phenylbutyl Ether (*E*-4j)
IR (neat): 3027, 2955, 2861, 1631, 1496, 1454, 1379, 1363, 1238, 1134, 1048, 862, 747, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.18 (d, *J* = 6.6 Hz, 6 H), 1.23–1.36 (m, 2 H), 1.42–1.52 (m, 2 H), 1.60–1.76 (m, 4 H), 2.22 (t, *J* = 7.5 Hz, 2 H), 2.64 (t, *J* = 7.2 Hz, 2 H), 2.92 (sep, *J* = 6.7 Hz, 1 H), 3.79 (t, *J* = 6.1 Hz, 2 H), 6.38 (s, 1 H), 7.16–7.20 (m, 3 H), 7.25–7.30 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.0, 22.3, 22.8, 27.6, 29.2, 29.3, 30.0, 35.3, 35.5, 72.3, 111.5, 125.8, 128.3, 128.4, 142.1, 150.7.

Anal. Calcd for $C_{19}H_{30}OS$: C, 74.45; H, 9.87. Found: C, 74.74; H, 10.00.

(*Z*)-2-(Isopropylthio)hex-1-enyl 4-Phenylbutyl Ether (*Z*-4j)
IR (neat): 3026, 2956, 2927, 2861, 1639, 1496, 1453, 1380, 1363, 1154, 1051, 746, 698 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.19–1.34 (m, 2 H), 1.22 (d, *J* = 6.6 Hz, 6 H), 1.41–1.50 (m, 2 H), 1.63–1.74 (m, 4 H), 2.03 (t, *J* = 7.3 Hz, 2 H), 2.64 (t, *J* = 7.1 Hz, 2 H), 3.32 (sep, *J* = 6.6 Hz, 1 H), 3.81 (t, *J* = 6.1 Hz, 2 H), 6.27 (s, 1 H), 7.20–7.16 (m, 3 H), 7.25–7.30 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 13.9, 22.1, 23.1, 27.5, 29.3, 30.8, 33.6, 34.6, 35.5, 72.4, 109.6, 125.7, 128.3, 128.4, 142.1, 146.7.

(*E*)-2-Ethoxy-3-phenylprop-1-enyl 3-Methylbut-3-enyl Ether (*E*-4k)
IR (neat): 3063, 3029, 2978, 2903, 1650, 1603, 1495, 1454, 1392, 1245, 1139, 1056, 891, 778, 733, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.20 (t, *J* = 7.0 Hz, 3 H), 1.76 (s, 3 H), 2.34 (t, *J* = 6.9 Hz, 2 H), 3.53 (s, 2 H), 3.59 (q, *J* = 6.9 Hz, 2 H), 3.73 (t, *J* = 6.9 Hz, 2 H), 4.75 (br s, 1 H), 4.80 (br s, 1 H), 5.84 (s, 1 H), 7.15–7.30 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 14.9, 22.7, 34.4, 37.7, 63.6, 71.2, 111.8, 125.8, 126.8, 128.1, 128.6, 139.5, 142.4, 146.0.

(*Z*)-2-Ethoxy-3-phenylprop-1-enyl 3-Methylbut-3-enyl Ether (*Z*-4k)
IR (neat): 3063, 3028, 2975, 2928, 1687, 1650, 1603, 1495, 1454, 1369, 1343, 1199, 1137, 1052, 891, 701 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 3 H), 1.75 (s, 3 H), 2.35 (t, *J* = 6.9 Hz, 2 H), 3.23 (s, 2 H), 3.78 (t, *J* = 7.1 Hz, 2 H), 3.87 (q, *J* = 7.0 Hz, 2 H), 4.73 (br s, 1 H), 4.78 (br s, 1 H), 5.47 (s, 1 H), 7.17–7.31 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 15.5, 22.7, 37.2, 37.7, 65.9, 71.1, 111.9, 126.2, 128.2, 128.7, 130.0, 138.1, 139.0, 142.2.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.74; H, 9.33.

2-[(3-Methylbut-3-enyl)oxymethylidene]-5-phenyloxolane (4l, Major Isomer)
IR (neat): 3068, 3031, 2938, 1650, 1496, 1453, 1375, 1200, 1136, 1028, 890, 756, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.77 (s, 3 H), 1.86–1.99 (m, 1 H), 2.33–2.43 (m, 1 H), 2.35 (t, *J* = 7.0 Hz, 2 H), 2.62–2.79 (m, 2 H), 3.74 (t, *J* = 6.9 Hz, 2 H), 4.75 (br s, 1 H), 4.80 (br s, 1 H), 5.15 (dd, *J* = 6.4, 7.9 Hz, 1 H), 6.17 (t, *J* = 2.1 Hz, 1 H), 7.27–7.37(m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 22.7, 25.4, 33.1, 37.6, 71.1, 82.6, 111.7, 123.4, 125.6, 127.7, 128.4, 142.5.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.33; H, 8.30.

2-[(3-Methylbut-3-enyl)oxymethylidene]-5-phenyloxolane (4l, Minor Isomer)
IR (neat): 3070, 3030, 2937, 1650, 1452, 1342, 1181, 1136, 1078, 1027, 943, 890, 754, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.77 (s, 3 H), 1.91–2.00 (m, 1 H), 2.33–2.44 (m, 1 H), 2.41 (t, *J* = 7.3 Hz, 2 H), 2.54–2.60 (m, 2 H), 3.84 (t, *J* = 7.3 Hz, 2 H), 4.75 (s, 1 H), 4.79 (s, 1 H), 5.29 (t, *J* = 6.7 Hz, 1 H), 5.42 (t, *J* = 1.6 Hz, 1 H), 7.24–7.34 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 22.9, 25.9, 33.7, 37.7, 71.2, 83.2, 111.7, 119.9, 125.6, 127.5, 128.3, 140.8.

(*E*)-2-Ethoxy-3-phenylprop-1-enyl 3-Phenethylbut-3-enyl Ether (*E*-4m)
IR (neat): 3083, 3062, 3026, 2978, 2928, 1645, 1602, 1496, 1454, 1246, 1139, 1055, 894, 744, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.20 (t, *J* = 7.0 Hz, 3 H), 2.34 (t, *J* = 8.2 Hz, 2 H), 2.38 (t, *J* = 7.0 Hz, 2 H), 2.75 (t, *J* = 8.1 Hz, 2 H), 3.53 (s, 2 H), 3.59 (q, *J* = 7.0 Hz, 2 H), 3.74 (t, *J* = 6.9 Hz, 2 H), 4.83 (br s, 1 H), 4.85 (br s, 1 H), 5.83 (s, 1 H), 7.15–7.30 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 14.8, 34.3, 34.4, 36.2, 38.1, 63.5, 71.4, 111.2, 125.81, 125.82, 126.8, 128.1, 128.3, 128.6, 139.5, 142.0, 145.7, 146.0.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.44; H, 8.51.

(*Z*)-2-Ethoxy-3-phenylprop-1-enyl 3-Phenethylbut-3-enyl Ether (*Z*-4m)
IR (neat): 3062, 3027, 2977, 2927, 1687, 1645, 1603, 1496, 1454, 1368, 1343, 1198, 1138, 1052, 894, 747, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.11 (t, *J* = 7.1 Hz, 3 H), 2.34 (t, *J* = 8.5 Hz, 2 H), 2.40 (t, *J* = 7.3 Hz, 2 H), 2.75 (t, *J* = 8.1 Hz, 2 H), 3.23 (s, 2 H), 3.79 (t, *J* = 7.1 Hz, 2 H), 3.86 (q, *J* = 7.0 Hz, 2 H), 4.81 (br s, 1 H), 4.84 (br s, 1 H), 5.46 (t, *J* = 0.83 Hz, 1 H), 7.15–7.31 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 15.5, 34.3, 36.2, 37.1, 38.1, 65.8, 71.2, 111.3, 125.8, 126.2, 128.2, 128.3, 128.7, 130.0, 138.1, 138.9, 141.9, 145.5.

(*E*)-2-Ethoxy-3-phenylprop-1-enyl 2-(Trimethylsilyl)ethyl Ether (*E*-4n)
IR (neat): 3029, 2978, 2953, 2896, 1603, 1495, 1454, 1250, 1136, 1113, 1056, 860, 837, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.95–1.01 (m, 2 H), 1.18 (t, *J* = 7.0 Hz, 3 H), 3.53 (s, 2 H), 3.57 (q, *J* = 7.0 Hz, 2 H), 3.68–3.71 (m, 2 H), 5.81 (s, 1 H), 7.11–7.29 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –1.1, 15.2, 18.6, 34.6, 63.8, 70.5, 126.1, 127.0, 128.4, 128.9, 139.9, 145.9.

Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.14; H, 9.77.

(*Z*)-2-Ethoxy-3-phenylprop-1-enyl 2-(Trimethylsilyl)ethyl Ether (*Z*-4n)
IR (neat): 3029, 2953, 2926, 2898, 1687, 1495, 1454, 1381, 1342, 1250, 1198, 1133, 1051, 860, 838, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.97–1.03 (m, 2 H), 1.10 (t, *J* = 7.0 Hz, 3 H), 3.21 (s, 2 H), 3.70–3.75 (m, 2 H), 3.85 (q, *J* = 7.0 Hz, 2 H), 5.44 (s, 1 H), 7.15–7.28 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –1.2, 15.7, 18.7, 37.3, 66.0, 70.3, 126.4, 128.5, 129.0, 130.3, 137.9, 139.3.

(*E*)-2-Ethylthio-3-phenylprop-1-enyl 2-(Trimethylsilyl)ethyl Ether (*E*-4o)
IR (neat): 3085, 3028, 2954, 1631, 1495, 1453, 1420, 1383, 1305, 1250, 1226, 1148, 1082, 1030, 838, 764, 719, 698, 627 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.97–1.03 (m, 2 H), 1.05 (t, *J* = 7.3 Hz, 3 H), 2.30 (q, *J* = 7.3 Hz, 2 H), 3.54 (s, 2 H), 3.88–3.93 (m, 2 H), 6.49 (s, 1 H), 7.09–7.24 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –1.4, 14.4, 18.6, 27.0, 35.4, 70.4, 109.4, 125.9, 128.1, 128.8, 140.2, 150.5.

Anal. Calcd for $C_{16}H_{26}OSSi$: C, 65.25; H, 8.90. Found: C, 65.48; H, 8.94.

(*Z*)-2-Ethylthio-3-phenylprop-1-enyl 2-(Trimethylsilyl)ethyl Ether (*Z*-4o)
IR (neat): 3027, 2954, 2925, 1638, 1495, 1453, 1382, 1250, 1147, 1031, 970, 938, 838, 757, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.04 (s, 9 H), 1.04–1.10 (m, 2 H), 1.13 (t, *J* = 7.3 Hz, 3 H), 2.60 (q, *J* = 7.4 Hz, 2 H), 3.41 (s, 2 H), 3.89–3.95 (m, 2 H), 6.34 (s, 1 H), 7.18–7.32 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –1.5, 14.7, 18.6, 25.7, 39.6, 70.4, 126.2, 128.2, 128.7, 147.1.

2-(*N*-Methyl-*N*-phenylamino)-2-phenylethenyl 2-(Trimethylsilyl)ethyl Ether (4p)
IR (neat): 3059, 3026, 2952, 2894, 2816, 1645, 1599, 1501, 1445, 1363, 1322, 1250, 1227, 1147, 1051, 1031, 955, 859, 837, 764, 748, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.98–1.04 (m, 2 H), 3.17 (s, 3 H), 3.94–4.00 (m, 2 H), 6.58 (s, 1 H), 6.64–6.74 (m, 3 H), 7.13–7.31 (m, 7 H).

^{13}C NMR ($CDCl_3$): δ = –1.5, 18.7, 38.0, 70.8, 112.7, 116.3, 124.7, 125.4, 126.4, 128.5, 128.7, 137.1, 142.3, 148.0.

Anal. Calcd for $C_{20}H_{27}ONSi$: C, 73.79; H, 8.36, N, 4.30. Found: C, 73.87; H, 8.32, N, 4.03.

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